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Sorptive removal of Ce(Ⅳ) from aqueous solution by bentonite

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Abstract

Bentonite has been studied extensively because of its strong adsorption capacity. A local bentonite named GMZ bentonite, collected from Gaomiaozi County (Inner Mongolia, China), was selected as the first choice of buffer/backfill material for the high-level radioactive waste repository in China. In this research, purification of raw bentonite was done to remove quartz. X-ray Diffraction(XRD) was used for the characterization of purified bentonite .In addition, the effects of contact time, solid dosage, pH, and temperature on Ce(IV) sorption to purified bentonite were also investigated by batch technique. The sorption kinetics and isotherms of bentonite for Ce(IV) indicate that the kinetic adsorption is well described by the pseudo-second-order model and the sorption isotherm is fitted well by Langmuir model. The equilibrium batch experiment data demonstrate that bentonite is effective adsorbent for the removal of Ce(IV) from aqueous solution.

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Keywords: Ce(Ⅳ); Sorption; Bentonite

1. Introduction

With the development of nuclear industry, nuclear technique has been widely used in many fields, such as national defense, industry, agriculture and medicine[1]. A large amount of radioactive waste is produced ,which contains a variety of radionuclides. The increasing level of harmful radionuclides discharged into the environment make great harm to natural environment and human society. So remove radionuclide from radioactive wastewater has special importance for all organism benefit from water. A variety of methods such as chemical precipitation[2,3], ion exchange[4] and sorption[5] are employed for removal radionuclides from aqueous solutions. A large number of domestic and international research shows, sorption is considered one of the best techniques in terms of cost,

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simplicity of design and operation, especially for effluents with moderate and low concentrations[6].

Bentonite has attracted great interest in nuclear waste management because of its outstanding properties. The prominent properties of chemical and mechanical stability, high specific surface area and high cation exchange capacity provide bentonite retardation for the transport of radionuclides from the repository to the environment. In this context, it is of great significance for design and security assessment of the repository to study the interaction between radionuclides and bentonite. In recent years, bentonite has been greatly studied for the removal of heavy metal ions and radionuclides [7-10]. However, the sorption of Ce(IV) and other trivalent lanthanides or actinides on bentonite is still scarce.

Ce(IV) has similar chemical properties with radioactive elements Pu(IV) because the ionic radius of Ce(IV) is almost the same for the trivalent lanthanides and actinides. The sorption of Ce(IV) on activated carbon [11], zeolite[12] had been studied, but no available study was focused on the sorption behaviors of Ce(IV) on bentonite. The main purposes of this work are: (1) prepare purified bentonite and characterize using X-ray Diffraction (XRD); (2) the effect of pH, contact time and temperature on Ce(IV) sorption on bentonite was studied in detail;(3) calculate the thermodynamic parameters of Ce(IV) adsorption on bentonite, such as ΔH°, ΔS° and ΔG°; (4) to discuss the sorption mechanism of Ce(IV) on bentonite.

2. Experimental

2.1. Materials

All reagents used in this study were of analytical grad reagents. Milli-Q water was used in all experiments. Ce(IV) stock solution was prepared by dissolving weighed amounts of ceric ammonium nitrate in Milli-Q water.

2.2. Purification of raw bentonite

The main aim of this purification is to remove impurities. This process was done using the following steps: at the beginning, 10g nature bentonite was mixed with Milli-Q water in proportion of 1:10 by weight and stirred with a high-speed (2000rpm) for 2 h. The suspensions standing for 24h, then upper suspensions were centrifuge at 7000rpm.The obtained solid was dried at 105℃for 2h in order to remove free water. At last, the sample was milled through a 200-mesh screen and used in the experiments.

2.3. Characterization

Structural characterization of bentonite was carried out by X-ray diffraction (XRD) in a diffractometer (X'Pert PRO, PANalytical, Holland) equipped with a Cu Ka radiation source between 3° and 80° at room temperature. The JCPDS PDF database was used for the phase identification.

2.4. Adsorption experiments

The sorption of Ce(IV) on bentonite was investigated by using batch technique in 250 mL stoppered conical flask under ambient conditions. The stock suspension of bentonite and $NaClO_4$ were pre-equilibrated for 24 h, then Ce(IV) stock solution was added in bentonite suspension to achieve the desired concentrations of different components. The mixtures were shaken by a constant-temperature shaker (IS-RDH1, Crystal, America) and then were centrifuged (TG1850-WS, Luxiangyi, Shanghai, China) at 7000 rpm for 30 min. The kinetics experiment were performed by mixing 0.1g bentonite with solutions of Ce(IV) (2.26 mmol/L).The mixtures were separated after shaking 0–24 h at 303 ± 1 K. Except when pH effect was studied, all experiments were carried out at initial pH = 1.8 ± 0.1. The pH was adjusted with 0.1 M perchloric acid and 0.01 M sodium hydroxide. In addition, the pH of the system was determined during the sorption process using an pH meter (S975 SevenExcellence, Mettler Toledo, Shanghai, China). Sorption isotherms were performed (T = 288, 303, 318 and333 ± 1 K), with an initial Ce(IV) concentration ranging from 1.52 to 4.28 mmol/L. The amounts of absorbed Ce(IV) were calculated from the difference between the equilibrium concentration (C_e) and the initial one (C_0), i.e., $C_s=(C_0-C_e)V/m$, where m (g) is the mass of bentonite and V (L) is the volume of the suspensions. The adsorption percentage

(sorption(%)=(C_0−C_e)/C_0×100%) was also obtained from the difference between C_e and C_0. All experimental data were the average of duplicate determinations and the relative errors were about 5%.

3. Results and discussion

3.1. Characterization of XRD

X-ray diffraction is a nondestructive analytical technique, which reveals information about crystallographic structure. The technique is widely used in the characterization of clays. The XRD patterns for raw bentonite and purified bentonite are shown in Fig. 1. This figure shows that the percent of quartz decreases significantly after purification process while the montmorillonite content increases.

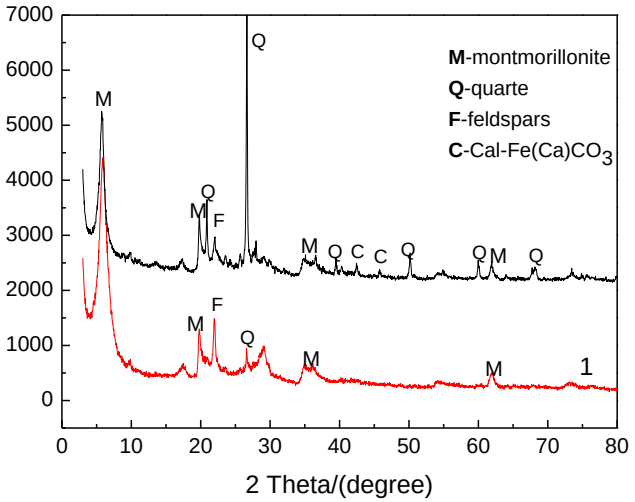

Fig. 1. XRD of purified bentonite (named 1) and natural bentonite (named 2).

3.2. Effect of contact time

The effect of time on sorption of Ce(IV) on bentonine was investigated because the equilibrium time is one of the important parameters. The sorption of Ce(IV) ions has been investigated on adsorbed as a function of time in the range of 5–180 min and the results are shown in Fig. 2.As can be seen from Fig. 2, it is observed that the sorption percentage increases rapidly in the first contact time of 40 min, and then maintains high level with increasing contact time. Therefore, the time of 2h is selected in the following experiments to ascertain that the sorption can achieve complete equilibrium.

In order to analyze the sorption rate of Ce(IV) on bentonine, a pseudo-second-order was applied to simulate the kinetic adsorption. The pseudo-second-order equation can be expressed as[13]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (1)$$

Where q_t is the amount of metal ions absorbed at time t (mg/g), q_t is the amount of metal ions absorbed at equilibrium (mg/g); K_2 (g/(mg·min)) is the pseudo-second-order rate constant. Linear plot feature of *t/qt* vs. *t* was shown in Fig. 3. The K_2 and q_e values calculated from the slope and intercept of the linear plots of *t/qt* versus t are

5.18×10^{-3} g/(mg·min) and 270.27 mg/g, respectively. The correlation coefficients (R^2=0.9999) of the pseudo-second-order rate equation for the linear plot is very close to 1, indicating that the kinetic sorption of Ce(IV) on bentonite is well described by the pseudo-second-order rate equation.

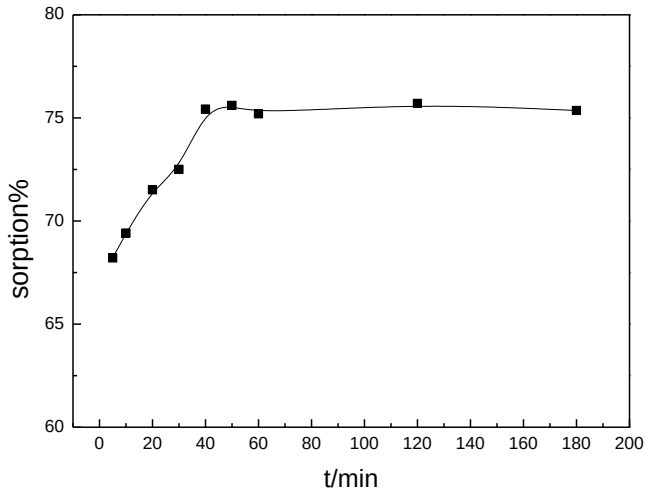

Fig. 2 Effect of contact time on the sorption of Ce(IV) on bentonite. pH=1.80±0.05,T=(303±0. 5)K,I=0.01M $NaClO_4$,m/V=0.8g/L,C_0(Ce(IV))= 2.26 mmol/L

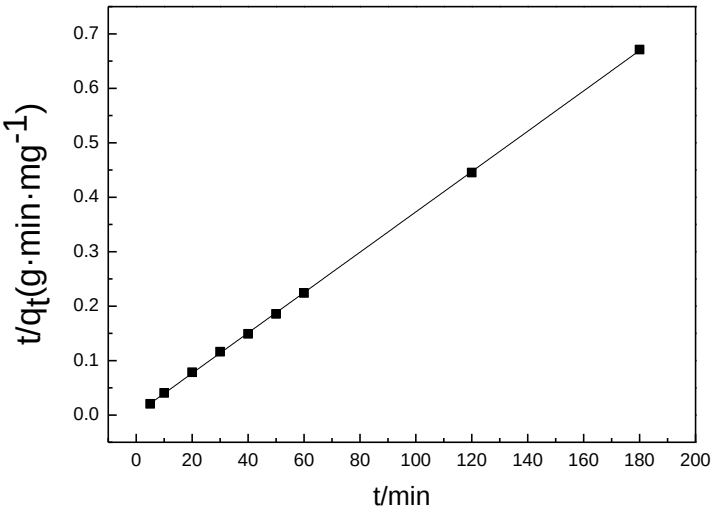

Fig. 3 The pseudo-second-order rate of Ce(IV) on bentonite. pH=1.80±0.05,T=(303±0. 5)K,I=0.01M $NaClO_4$,m/V=0.8g/L,C_0(Ce(IV))= 2.26 mmol/L

3.3. Effect of clay dosage

The sorption of Ce(IV) on bentonite as a function of bentonite dosage is shown in Fig. 4. The distribution of

the coefficient, K_d, values as a function of the bentonite dosage is also plotted in Fig. 4. The K_d value was derived from the following equation:

$$K_d = \frac{C_0 - C_e}{C_0} \times \frac{V}{m} \quad (2)$$

The sorption percentage of Ce(IV) from aqueous solution to bentonite increases with increasing bentonite dosage. This phenomenon is due to the amount of functional groups at bentonite surfaces increases with increasing clay dosage. Thereby, more surface sites are available for the sorption of Ce(IV) at higher clay dosage. One can see that, the distribution coefficient (*log* K_d, mL/g) decreases with increasing clay dosage. This may be attributed to the competition among the colloids of bentonite[14]. The results of the sorption of Co(II) [6] and Cd(II)[15] are very similar to the results of this work. At low bentonite dosage, Ce(IV) can easily access the sorption sites of bentonite and the sorption capacity is high. However, at high bentonite dosage, the competition among the colloids of bentonite reduce the effective sites and results in the decreases the sorption capacity of Ce(IV) on bentonite.

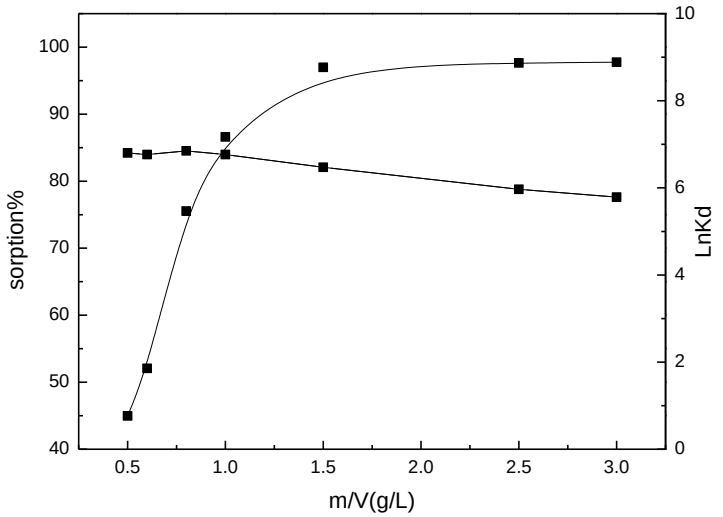

Fig.4. Effect of clay dosage on Ce(IV) sorption on bentonite. pH=1.80±0.05,T=(303±0. 5)K,I=0.01M $NaClO_4$,C_0(Ce(IV))= 2.26 mmol/L

3.4. Effects of pH

The pH value is one of the important parameter that influence the sorption of Ce(IV) from aqueous solutions by using batch technique. The sorption of Ce(IV) on bentonite were evaluated and presented as sorption percentage at various pH values. The results are shown in Fig. 5. A pronounced increase of Ce(IV) sorption from about 74% to 96% as pH increases from 1.80 to 4.00 and then maintains high level with increasing pH values. The strong pH dependent sorption of Ce(IV) on bentonite suggests that surface complexation contributes mainly to the sorption of Ce(IV) on bentonite[16-19].

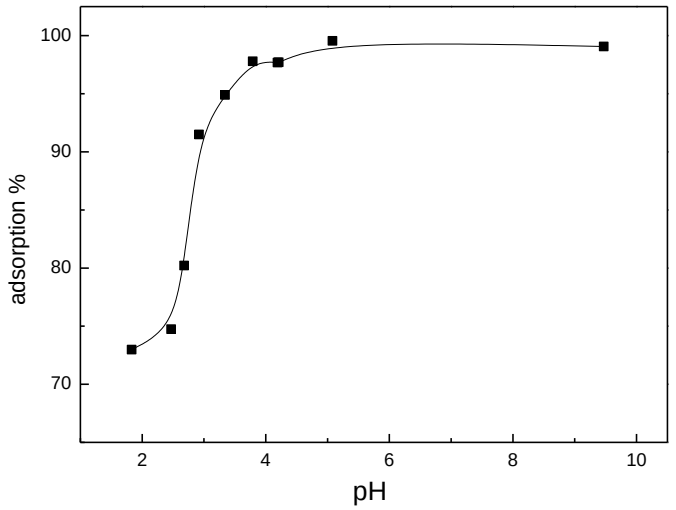

Fig.5. Effect of pH on Ce(IV) sorption on bentonite. T=(303±0. 5)K,I=0.01M $NaClO_4$,m/V=0.8g/L,C_0(Ce(IV))= 2.26 mmol/L

3.5. Sorption isotherms and thermodynamic parameters

For the sake of understanding the sorption mechanism, the sorption experiments were performed using different initial concentrations of Ce(IV) at four different temperature(288,303,318,333 ± 1K) to achieve the sorption isotherm. From the available isotherm models Langmuir and Freundlich were selected to be studied in this work.

The Langmuir isotherm model is commonly used to describe monolayer sorption process onto a surface. Its form can be expressed by the following equation[20]:

$$\frac{C_e}{C_s} = \frac{C_e}{C_{\max}} + \frac{1}{C_{\max} K_L} \tag{3}$$

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

where C_{max}(mol/g), the maximum sorption capacity, is the amount of adsorbate at complete monolayer coverage, q_e(mol/g) is the equilibrium sorption capacity, and K_L(L/mol) is the Langmuir constant that relates to the heat of sorption. The values of R_L indicate the type of Langmuir isotherm to be either irreversible (R_L=0), favorable (0 <R_L< 1), liner (R_L=1) or unfavorable (R_L> 1)[11]. The plots of C_e/Cs versus C_e for the sorption of Ce(IV) on bentonine for Ce(IV) solution concentrations ranging from 1.52 to 4.28 mmol/L at four different temperature(288,303,318,333±1K).

Unlike the Langmuir model, the Freundlich isotherm is an empirical equation employed to describe equilibrium on heterogeneous surfaces. The model equation[21]:

$$\log C_S = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where K_F(mol^{1-n} • L^n/g) is roughly an indicator of the adsorption capacity and *1/n* is the degree of heterogeneity of sorbent. The Freundlich parameters (K_F and *n*) indicate whether the nature of sorption is either favorable or unfavorable. The data obtained from the sorption of Ce(IV) on bentonine were fitted to the Freundlich model by plotting *lnCs* versus *lnCe*.

Fig.6 shows the experimental sorption isotherms of Ce(IV) on bentonine at four different temperature(288,303,318,333±1K). One can see that the sorption decreases with rise in temperature. The Langmuir and Freundlich sorption isotherms of Ce (IV) at the four different temperatures were given in Fig. 7and Fig.8. The relative parameters calculated from the two models are listed in Table 1. As can be seen from the correlation coefficients that Langmuir model simulates the experimental data better than Freundlich models, which indicates that almost complete monolayer coverage of the bentonite particles. In the Langmuir isotherm model, the dimensionless parameter(R_L) values between 0 and 1, pointing out that sorption process of Ce(IV) ions on bentonite is favourable[8]. The maximum sorption (C_{max}) acquired from the Langmuir model were found to decrease with an increase in the solution temperatures from 288 to 333 K, which suggests that sorption process of Ce(IV) on bentonine was exothermic.

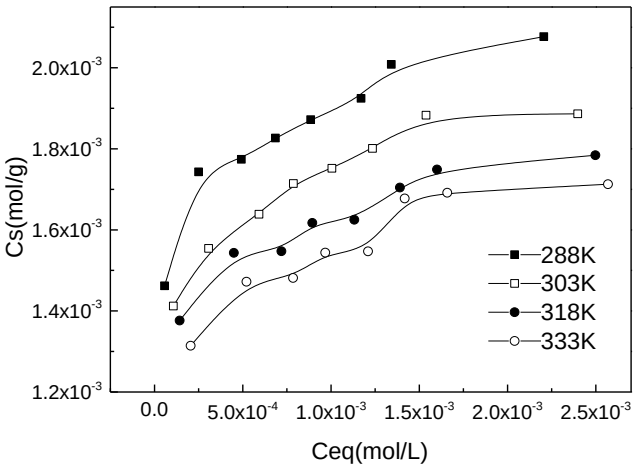

Fig. 6 Sorption isotherms of Ce(IV) on bentonite at four different temperatures. pH=1.80±0.05 ,I=0.01M $NaClO_4$,m/V=0.8g/L

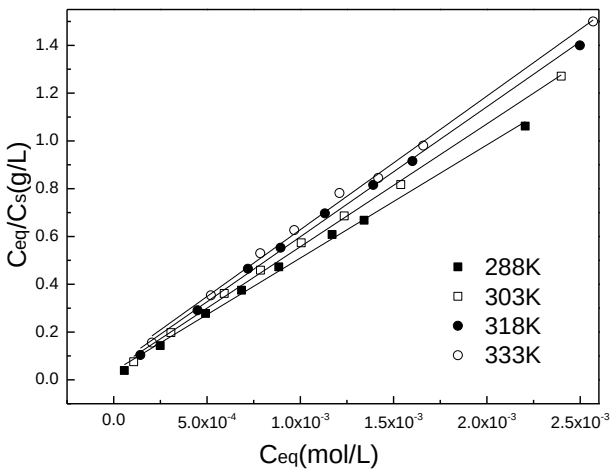

Fig. 7 Langmuir plots of Ce(IV) on bentonite at four different temperatures. pH=1.80±0.05 ,I=0.01M $NaClO_4$,m/V=0.8g/L

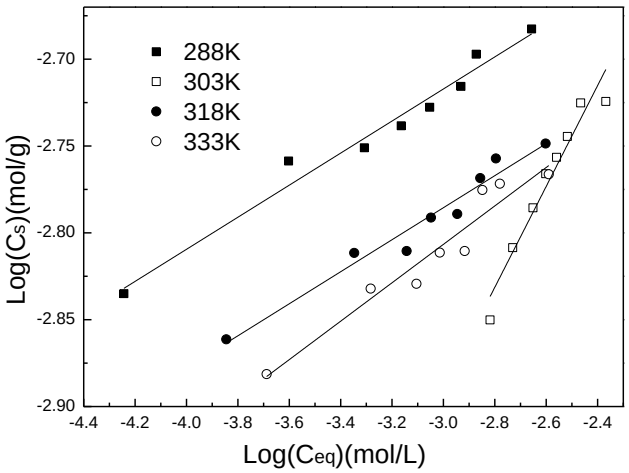

Fig. 8 Freundlich plots of Ce(IV) on bentonite at four different temperatures. pH=1.80±0.05 ,I=0.01M $NaClO_4$,m/V=0.8g/L

Table 1. The parameters for Langmuir and Freundlich isotherms

Models	parameters				
	T/(*K*)	K_L(*L*·*mol*$^{-1}$)	R_L	C_{max}（*mol*·*g*$^{-1}$）	R^2
Langmuir	288	1.30×10^{4}	0.048-0.017	2.11×10^{-3}	0.996
	303	1.20×10^{4}	0.052-0.019	1.95×10^{-3}	0.994
	318	9.98×10^{3}	0.062-0.023	1.84×10^{-3}	0.995
	333	8.08×10^{3}	0.075-0.028	1.79×10^{-3}	0.994
	T/(*K*)	K_F(*mol*$^{1-n}$·*L*^{n}·*g*$^{-1}$)		*1/n*	R^2
Freundlich	288	3.63×10^{-3}		0.092	0.969
	303	9.53×10^{-3}		0.290	0.935
	318	3.09×10^{-3}		0.092	0.954
	333	3.39×10^{-3}		0.111	0.924

The thermodynamic parameters, free energy change ($\triangle G°$), enthalpy change ($\triangle H°$) and entropy change ($\triangle S°$), were calculated from the temperature dependent adsorption isotherms. The thermodynamic parameters ($\triangle H°$, $\triangle S°$ and $\triangle G°$) were calculated by the following equation[22]:

$$\Delta G^0 = -RT\ln K^0 \tag{6}$$

$$\ln K^{O} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{7}$$

where K^0 is the sorption equilibrium constant. Value of K^0 is the Langmuir constant K_L that in different temperature[23,24]. The $\triangle H°$ and $\triangle S°$ parameters can be calculated from the slope and intercept of the plot of *ln* K_L versus *1/T* yields, respectively. Relevant parameters calculated from Eqs. (6) and (7) are summarized in Table 2. A negative value of the standard enthalpy change indicates that the sorption process is exothermic. $\triangle G°$ are negative as expected for a spontaneous process. The decrease of $\triangle G°$ with the increase of temperature indicates that the reaction is more efficient at lower temperature[25]. The positive values of entropy change ($\triangle S°$) reflects the affinity of the adsorbent toward Ce(IV) ions in the solutions and may suggest some structural changes in the bentonite[26].

Table 2.Values of thermodynamic parameters for the sorption of Ce(IV) on bentonite.

T/K	lnK_L	$\triangle G°/(kJ·mol^{-1})$	$\triangle S°/(J·mol^{-1}·K^{-1})$	$\triangle H°/(kJ·mol^{-1})$
288	9.48	-22.69	49.51	-8.52
303	9.39	-23.66		
318	9.20	-24.34		
333	9.00	-24.91		

4. Conclusion

From the results of Ce(IV) sorption on bentonite at different experimental conditions, one can draw the following conclusions:

1. The sorption of Ce(IV) on bentonite is rather quickly and the kinetic sorption can be described by the pseudo-second-order model very well.

2. Sorption of Ce(IV) on bentonite is strongly dependent on pH values, and the sorption of Ce(IV) on bentonite increased with the increase of pH 1.8-4.

3. The sorption of Ce(IV) on bentonite can be described by Langmuir models well. The thermodynamic derived from temperature dependent sorption isotherms suggest that the sorption reaction is spontaneous and exothermic process.

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